

# Coexistence of Haldane gap excitations and long-range order in $R_2\text{BaNiO}_5$ ( $R$ =rare earth)

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## Abstract

$R_2\text{BaNiO}_5$  ( $R$  = rare earth) quasi-1-D antiferromagnets are structurally equivalent to the well-studied 1-D  $S = 1$  Haldane-gap compound  $\text{Y}_2\text{BaNiO}_5$ . Unlike the Y-nickelate though, these materials undergo 3-D magnetic ordering at finite temperatures. Recent inelastic neutron scattering studies of  $\text{Pr}_2\text{BaNiO}_5$  and  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  revealed purely 1-dimensional gap excitations that propagate exclusively on the Ni-chains and are strikingly similar to Haldane gap modes in  $\text{Y}_2\text{BaNiO}_5$ . In the ordered phase these excitations survive and actually coexist with conventional spin waves. The results suggest that the Haldane singlet ground state of the Ni-chains is not fully destroyed by Néel ordering.

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In 1983 the pioneering theoretical work by Haldane[1] has radically changed our understanding of low-dimensional (low-D) quantum magnetic system. It was suggested that the static and dynamical properties of a simple 1-D Heisenberg antiferromagnet (AF) are totally different for integer and half-integer spin models: for *integer* spins the ground state is a non-magnetic singlet, the excitation spectrum has a *gap* and the spin correlations decay exponentially over a length of only several lattice units. The excitations are a  $S = 1$  triplet with an energy minimum at the 1-D AF zone-center  $Q = \pi a^*$ , where  $2\pi/a^*$  is the in-chain lattice constant. Haldane's conjecture is now supported by a vast amount of theoretical and numerical results. Most important, in quite a few real 1-D integer-spin systems the singlet ground state and Haldane gap excitations have been observed and studied experimentally. Comprehensive lists of references may be found in several recent publications, as for example in Refs. [2–6].

In the *quasi*-1-D case, when magnetic interactions between adjacent integer-spin chains are finite, we can still expect a quantum-disordered singlet ground state with a spin gap in the limit of very weak coupling. For strong inter-chain interactions the system becomes 3-dimensional, the ground state is Néel-like,

and the excitations are conventional spin waves with no energy gap. The most physically interesting case is that of intermediate coupling strengths. A great deal of work aimed at understanding this situation was done on  $\text{CsNiCl}_3$  and related compounds (see for example Refs. [7–10] and references therein). In the present paper we discuss recent experimental results obtained for a different family of *quasi*-1-D antiferromagnets, namely those with the general formula  $R_2\text{BaNiO}_5$ , where  $R$  stands for one of the rare earth elements or Y. The most important structural feature of these systems are parallel chains of  $\text{Ni}^{2+}$  ions running along the  $a$  axis of the orthorhombic crystal structure (See Fig. 1 in Refs. [11,12]). The  $S = 1$   $\text{Ni}^{2+}$  ions are linked via the apical oxygen sites of their coordination octahedra, which results in relatively strong in-chain AF interactions with  $J \approx 25$  meV. The chains are structurally separated from one another, and the  $R^{3+}$  sites are positioned between the chains. Both Ni-O- $R$  and  $R$ -O- $R$  superexchange routes may be active, and in the case when  $R^{3+}$  is a magnetic rare earth ion the system orders antiferromagnetically with  $T_N$  ranging from 24 K to almost 80 K [13–18]. However, if  $R = \text{Y}$  the chains are magnetically isolated. No long-range order has been found so far in  $\text{Y}_2\text{BaNiO}_5$ , while Haldane gap excitations have been observed [19] and studied in great detail [5,20].  $R_2\text{BaNiO}_5$  species thus appear to be almost ideal model materials for studying the cross-over from 1-D quantum to 3-D classical behavior: i) in contrast to  $\text{CsNiCl}_3$ , where the chains form a frustrated 2-D triangular lattice, in  $R_2\text{BaNiO}_5$  there is no obvious frustration of inter-chain interactions that could complicate the picture; ii) the Haldane gap  $\Delta \approx 10$  meV in  $\text{Y}_2\text{BaNiO}_5$  is in the energy range readily accessible in neutron scattering experiments; iii) compounds with different  $R$  substitutes have different magnetic structures and ordering temperatures, which allows to separate common behaviour from that characteristic of a particular species; and iv) by preparing samples with different proportions of magnetic rare earths and non-magnetic Y, the experimentalist obtains a *direct handle* on the strength of inter-chain coupling.

In many ways the  $R_2\text{BaNiO}_5$  ( $R \neq \text{Y}$ ) compounds behave as good 3-D classical antiferromagnets. Bulk properties and magnetic structures were investigated for  $R = \text{Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er}$  and Tm, using standard magnetic techniques [15–17], neutron diffraction [13,14,11,18,21], and even resonant magnetic X-ray scattering [22]. In all compounds the Néel temperatures are smaller than the in-chain exchange constant by less than an order of magnitude. The temperature dependence of magnetic moments is rather well described by mean-field models. No deviations of the order-parameter critical exponent  $\beta$  from the Ginsburg-Landau value  $\beta = 0.5$  have been found so far. The only hint of some low-D and quantum behavior is a suppressed saturated moment of the Ni ions, typically  $1.1 \mu_B$ , as compared to the classical value of  $2 \mu_B$ . Two types of magnetic structures with propagation vectors  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  exist [13,14]. In  $\text{Er}_2\text{BaNiO}_5$  the spins are almost parallel to the chain direction ( $a$  axis). [13] In most other materials, such as  $\text{Nd}_2\text{BaNiO}_5$  and  $\text{Pr}_2\text{BaNiO}_5$ , both  $\text{Ni}^{2+}$  and  $R^{3+}$  moments are confined to the  $(b, c)$  crystallographic plane

[11,12,18]. The structure is non-colinear in the latter case [18], but is roughly as shown in Fig.3 in Ref. [11]. What is important for the following discussion is that in all  $R_2\text{BaNiO}_5$  species both  $\text{Ni}^{2+}$  and  $R^{3+}$  moments order simultaneously, i.e., with a single Néel temperature.

If  $R_2\text{BaNiO}_5$  ( $R \neq \text{Y}$ ) are, indeed, almost-classical systems, are the purely quantum-mechanical integer-spin dynamics totally destroyed? Or do the spin-singlet state of the Ni chains and the Haldane-gap excitations somehow survive in the magnetically ordered species? The main goal of this paper is to argue that it is the latter, the more physically interesting scenario that is realized. The first evidence for this were obtained in single-crystal inelastic neutron scattering experiments on  $\text{Pr}_2\text{BaNiO}_5$  [12]. The material orders magnetically in a  $\text{Nd}_2\text{BaNiO}_5$ -type structure at  $T_N = 24$  K. Above this temperature, at  $T = 30$  K, an inelastic peak centered around 12 meV is observed in constant- $Q$  scans at the 1-D AF zone center  $(1.5, 0, 0)$  [Fig. 1(a)]. Careful measurements at different wave vectors have shown that this excitation is virtually identical to Haldane gap excitations in  $\text{Y}_2\text{BaNiO}_5$ : (1) The dispersion is very steep along the chain direction, and has minima at  $Q_{\parallel} = Q_{\parallel}^{(n)} \equiv (2n + 1)\pi a^*$ , where the subscript “ $\parallel$ ” indicates a projection on the  $a$  axis and  $n$  is integer. Around its minima the dispersion is parabolic and can be approximated as  $(\hbar\omega_{\mathbf{Q}}) = \Delta^2 + c_0^2(Q_{\parallel} - Q_{\parallel}^{(n)})^2$ , where  $\Delta$  is the spin gap energy, and  $c_0$  is the spin wave velocity. A complete 3-axis deconvolution analysis of a set of constant- $Q$  scans yielded  $\Delta = 10.4(0.1)$  meV and  $c_0 = 200(11)$  meV Å at  $T = 30$  K. We see that the gap is very similar to that in the Y-nickelate. Moreover, knowing  $c_0$  allows us to determine the in-chain exchange constant  $J = c_0/(2.7a) \approx 223$  K, also close to  $J = 285$  K in  $\text{Y}_2\text{BaNiO}_5$ . (2) The transverse dispersion is almost zero. In fact, it is at least an order of magnitude too small to induce any long-range order through softening of Haldane excitations at the 3-D AF zone center,[23] as is the case in  $\text{CsNiCl}_3$ , for example. (3) The energy-integrated intensity of the excitation decreases rapidly as one moves away from the 1-D AF zone centers. The measured dynamic structure factor  $S(\mathbf{Q}, w)$  can be accurately fit [Fig. 1, solid lines] to the double Lorentzian (DL) form (Eq. 3 in Ref. [4]), predicted for Haldane-gap excitations. The fitting procedure yields a value for the in-chain correlation length  $\xi$  which, to within experimental errors, satisfies the relation  $\Delta \approx c_0/\xi$ , expected for Haldane-gap systems [24,25]. (4) Measurements in different Brillouin zones have shown that the energy-integrated intensity of the inelastic peak depends only on  $Q_{\parallel}$ . The dynamic structure factor is purely 1-D and shows no 3-D intensity modulation expected from Ni-Pr interference. Thus the gap excitations propagate *exclusively* on the Ni-sites, without any involvement of the Pr spins. In other words, as long as the system is in the paramagnetic phase, the dynamics of the Ni-spins do not depend on the properties of the  $R$ -substitute, and it is natural to assume that in  $\text{Pr}_2\text{BaNiO}_5$ , just as in  $\text{Y}_2\text{BaNiO}_5$ , we are looking at real Haldane-gap excitations propagating on the  $\text{Ni}^{2+}$  chains. The most exciting result is that below  $T_N$ , i.e., in the magnetically ordered state,

the Ni-chain excitations survive [Fig. 1(b)]. As will be discussed in detail below, the gap energy increases, while the intensity is decreased. The point to be emphasized here is that the change in excitation energy is *not* due to an increase in the transverse dispersion of the gap modes, as in  $\text{CsNiCl}_3$  [7,26]: the whole dispersion surface goes up, *independently* of the momentum transfer perpendicular to the chain direction. In fact, *all* the 1-D features discussed in the previous paragraph, including the Ni-chain-only structure factor are preserved. Conventional acoustic spin waves, i.e. Goldstone modes associated with long-range magnetic order, were also observed: they are separate entities and coexist with the Ni-chain gap modes. Unlike the latter however, the acoustic spin waves represent correlated spin fluctuations of *both* Ni and  $R$  moments. Their intensity varies significantly from one 3-D Brillouin zone to the next, and the overall intensity pattern follows that of the magnetic Bragg reflections.

We now turn to discussing the results obtained for  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  [27,21]. While no single-crystal data is available for these materials at the moment, inelastic neutron scattering experiments on powder samples have provided detailed information on the temperature dependence of the energy gap and on the effect of Y-substitution. For  $x = 1, 0.75, 0.5$ , and  $0.25$  the compounds order magnetically with  $T_N = 48, 39, 29.5$ , and  $19$  K, respectively. The saturation moment of the Ni-sublattice in all cases with  $x \geq 0.5$  is about  $1.1\mu_B$ . Observing the Haldane gap modes in powder samples is quite possible, thanks to the 1-dimensionality of the system. A typical constant-energy scan taken at the gap energy  $\Delta = 10$  meV in  $(\text{Nd}_{0.5}\text{Y}_{0.5})_2\text{BaNiO}_5$  is shown in Fig. 2(a) and has the characteristic saw-tooth shape produced when the DL 1-D structure factor is averaged over the direction of the scattering vector  $\mathbf{Q}$  [19,27] [solid lines in Fig. 2]. At  $|Q| > Q_{\parallel}^0$  a peak in constant- $Q$  scans is always observed at the gap energy  $\Delta$  [Fig. 2(b)].

By measuring the temperature dependence of the gap energy in samples with different Y-content and Néel temperatures we can finally observe, step by step, how the transition from the purely 1-D quantum-disordered case of  $\text{Y}_2\text{BaNiO}_5$  to the magnetically ordered case of  $\text{Nd}_2\text{BaNiO}_5$  occurs. Figure 3(a) summarizes the temperature evolution of the gap energy in several  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  samples, including the pure Y-nickelate ( $x = 0$ ) [20]. One readily sees the “universal” features: (1) In the paramagnetic phase, as far as the Ni-chain modes are concerned, there is virtually no difference between samples with different  $R \neq Y$  content. The gradual increase of the gap energy with temperature is a well-known intrinsic property of the 1-D  $S = 1$  Heisenberg model [28], and has been previously seen in several Haldane-gap compounds experimentally [29,6], including  $\text{Y}_2\text{BaNiO}_5$  [20]. (2) In the ordered phase the gap starts to increase, and the increase is linear with  $(T_N - T)$ . This is a totally new effect that has also been found in single-crystal measurements on  $\text{Pr}_2\text{BaNiO}_5$  [12]. (3) The temperature dependence of the energy-integrated

intensity in the gap excitations also shows some universal features: it decreases at high and low temperatures, extrapolates to a finite value at  $T = 0$  and is always a maximum at  $T \approx T_N$  [21].

How can we account for the presence of Haldane gap excitations propagating on the Ni-chains in a system that is not only magnetically ordered in 3 dimensions, but where the ordered moment on the chain sites is substantial? We suggest that in  $R_2\text{BaNiO}_5$  the inter-chain interactions are not sufficiently strong to destroy the Haldane singlet ground state of the individual  $S = 1$  chains. Magnetic ordering can be understood if one considers singlet-ground-state Ni-chains that get *polarized* by an effective staggered exchange field produced by the ordered  $R$ -sublattice [12,27]. Indeed, for a  $S = 1$  1-D AF, the dynamic structure factor at  $Q_{\parallel} = \pi a^*$  is non-zero, the static staggered susceptibility is also finite, and hence any staggered field will induce a finite staggered magnetization. Of course, since both Ni and  $R$  are essential for establishing a 3-D spin network [12], the problem is to be treated self-consistently, which will automatically explain why the Ni and  $R$ -spins order simultaneously. Interestingly, this simple scenario can also explain the increase of the Haldane gap energy in the ordered phase. Recently S. Maslov [30] has performed a rigorous theoretical analysis of our “staggered field” model and shown that the change in the gap energy below  $T_N$  should be quadratic with the staggered magnetization induced on the Ni-chains. Let's assume that the temperature dependence of the Ni moments is a function of  $T/T_N$  alone. This is a crude approximation, yet it is consistent with some preliminary data [21]. Noting that the saturation Ni moment in  $\text{Pr}_2\text{BaNiO}_5$  and  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  (except  $x = 0.25$ , where it has not yet been measured) are almost equal, we can expect the change in  $\Delta$  below  $T_N$  to be a universal function of  $(T/T_N)$  in *all* these systems. This conjecture is indeed consistent with experiment: Fig. 3(b) shows the increase of the spin gap in  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  and  $\text{Pr}_2\text{BaNiO}_5$  compared to that in  $\text{Y}_2\text{BaNiO}_5$  plotted against  $(T/T_N)$ . We see that all the experimental points fall on a single master curve. More accurate measurements of the  $T$ -dependencies of the sublattice magnetizations and gap energies in  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$ ,  $\text{Pr}_2\text{BaNiO}_5$  and other systems will in the future enable us to draw more quantitative conclusions.

In conclusion, a large amount of experimental data on magnetic excitations in  $R_2\text{BaNiO}_5$  systems has been accumulated so far. A consistent theoretical understanding of the remarkable coexistence of long-range order and Haldane-gap excitations is emerging. Nevertheless, many unanswered questions still remain and further work is required. A top priority is to verify the triplet nature of the Ni-chain excitations and measure the temperature dependence of the gap separately for each component. Conventional spin waves in  $R_2\text{BaNiO}_5$  compounds should be studied in greater detail. Systems like  $\text{Er}_2\text{BaNiO}_5$  should also be investigated, since they have different magnetic structures and may exhibit different behavior. Finally, if the model presented above is correct, in isomorphous *half-integer*-spin systems like  $\text{Nd}_2\text{BaCoO}_5$  [31] the gap excitations

should be totally absent, but only preliminary results exist now to confirm this conjecture [32].

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Fig. 1. Example constant- $Q$  scans showing the Ni-chain gap excitations in single-crystal  $\text{Pr}_2\text{BaNiO}_5$  measured above (a) and below (b) the Néel temperature  $T_N = 24$  K (from Ref. [12]).

Fig. 2. Example constant- $E$  (a) and constant- $Q$  (b) scans showing the Ni-chain gap excitations in  $\text{NdYBaNiO}_5$ . The measurements were done on a powder sample above the magnetic ordering temperature  $T_N = 29.5$  K (from Ref. [21]).

Fig. 3. a) Temperature dependence of the Haldane gap energy measured in several  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  powder samples (data from Refs. [27,21]). b) Haldane gap energies in several  $(\text{Nd}_x\text{Y}_{1-x})_2\text{BaNiO}_5$  and  $\text{Pr}_2\text{BaNiO}_5$  compounds plotted against  $T/T_N$ . The data are taken from Refs. [12,27,21].





